(19) World Intellectual Property Organization International Bureau



- 1 (16) 1

(43) International Publication Date 26 July 2001 (26.07.2001)

PCT

(10) International Publication Number WO 01/53895 A1

(51) International Patent Classification7:

G03G 9/13

(21) International Application Number: PCT/IL00/00031

(22) International Filing Date: 17 January 2000 (17.01.2000)

(25) Filing Language:

English

(26) Publication Language:

English

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:

ÙS

08/203,596 (CIP)

Filed on

28 February 1994 (28.02.1994)

- (71) Applicant (for all designated States except US): INDIGO N.V. [NL/NL]; 5, Limburglaan Street, NL-6221 SH Maastricht (NL).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): BEN AVRAHAM, Peretz [IL/IL]; Habosem Street 8, 76350 Rehovot (IL). BOSSIDAN, Becky [IL/IL]; Hatizmoret Street 46, 75573 Rishon Lezion (IL). LANDA, Benzion [IL/IL]; Itamar Ben Avi Street 26, Kfar Aharon, 74051 Nes Ziona (IL).

- (74) Agents: FENSTER, Paul et al.; Fenster & Company Patent Attorneys, Ltd., P.O. Box 10256, 49002 Petach Tikva (IL).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

01/53895 A1

(54) Title: LIQUID TONER AND METHOD OF PRINTING USING SAME

(57) Abstract: A liquid toner comprising: a carrier liquid; and toner particles dispersed in the carrier liquid, said toner particles comprising: a polymer blend comprising: a first polymer comprising a minor portion of said blend and having a relatively higher chemical reactivity with paper; and a second polymer comprising a major portion of said blend and having a relatively lower or null chemical reactivity with paper.

LIQUID TONER AND METHOD OF PRINTING USING SAME FIELD OF THE INVENTION

The present invention is related to the field of electrostaographic printing and especially to the field of printing using liquid toner.

BACKGROUND OF THE INVENTION

5

10

15

20

25

30

Modern liquid toner electrostatic imaging began with the invention of a new class of toners referred to herein as ElectroInk® (which is a trademark of Indigo, N.V. of The Netherlands). This toner is characterized by its comprising toner particles dispersed in a carrier liquid, where the toner particles are comprised of a core of a polymer with fibrous extensions extending from the core. When the toner particles are dispersed in the carrier liquid in a low concentration, the particles remain separate. When the toner develops an electrostatic image the concentration of toner particles increases and the fibrous extensions interlock. A large number of patents and patent applications are directed toward this type of toner and charge directors which are comprised in it. These include: US Patents 4,794,651; 4,842,974; 5,047,306; 5,407,307; 5,192,638; 5,208,130; 5,225,306; 5,264,312; 5,266,435; 5,286,593; 5,300,390; 5,346,796; 5,407,771; 5,554;476; 5,655,194; 5,792,584 and 5,5923,929, PCT Patent publication WO/92/17823 (equivalent to US Patent application 08/203,596) and PCT patent application PCT/IL99/00394, the disclosures of all of which are incorporated herein by reference.

It has been discovered that this type of toner allows for high quality offset printing at high speed. However, this type of printing is described *inter alia* in patents and patent application numbers 4,678,317; 4,860,924; 4,980,259; 4,985,732; 5,028,964; 5,034,778; 5,047;808; 5,078,504; 5,117,263; 5,148,222; 5,157,238; 5,166,734; 5,208,130; 5,231,454; 5,255.058; 5,266.435; 5,268,687; 5,270,776; 5,276,492; 5,278,615; 5,280,326; 5,286.948; 5,289,238; 5,315.321; 5,335,054; 5,337,131; 5,376,491; 5,380,611; 5,426,491; 5,436,706; 5,497,222; 5,508.790; 5,527,652; 5,552,875; 5,555,185; 5,557,376; 5,558,970; 5,570,193; 5,571,645; 5,732,274; 5,585,900; 5,592,269; 5,596,396; 5,610,694; 5,636,349; 5,655,194; 5,737,666; 5,745,829; 5,749,032; 5,793,490; 5,854,960; 5,864,353; 5,900,003; 5,915,152; 5,923,929; 5,935,754 and PCT publications (now US patent applications) WO 96/29633 (08/930,249); WO 96/35182 (08/945,415); WO 96/29633 (08/894,707); WO 97/07433 (09/011,634); WO 97/39385 (09/171,396); WO 98/55901 (09/445,035) and WO 99/454,433 and PCT applications PCT/IL98/00553 and PCT/IL99/00363, the disclosures of all of which

are incorporated herein by reference. Systems incorporating various ones of these patents are sold under the names E-Print 1000[®], Omnius[®], TurbostreamTM and CardpressTM.

In the course of time various methods for development of latent electrostatic images have been developed for liquid toner, as described in the above referenced patents and patent applications. In addition, the speed of printing has increased. Printing is performed on a large number of materials. Other operating conditions have also changed.

5

10

15

20

25

30

In general, ElectroInk comprises a polymer or polymers (usually pigmented) which solvate the carrier liquid at some temperature above room temperature (and preferably above normal storage temperatures of 30-40°C) and do not solvate the carrier liquid or dissolve substantial amounts of it below that temperature. Above the solvation temperature the polymer adsorbs the carrier liquid and is plasticized and softened by it. At elevated temperatures the toner material is thus soft enough to bond with a paper substrate. In practice, the temperature and pressure at which transfer to paper is made is controlled so that the transfer is complete, the transferred toner is fixed to the paper and the image is not squashed.

PCT publication WO 92/17823 (US Patent Application 08/203,596) discloses a toner comprising two components in which the viscosity vs. temperature characteristics are specified. In particular, it was found that toner based on a mixture of polymers having a break-point on a semi-logarithmic plot of viscosity vs. temperature at between 3x10⁵ and 5x10⁶ at a temperature of below 65°C, when in a 40% by weight of toner polymer mixed with carrier liquid, allowed for good transfer and fixing of the image at relatively low transfer blanket temperatures. This weight percentage was chosen as a standard since it represented a proportion believed to exist during transfer of the toner to a paper substrate.

SUMMARY OF THE INVENTION

An aspect of some preferred embodiments of the invention is concerned with liquid toners comprising pigmented toner particles in a carrier liquid. Preferably, the polymer in a 40% weight to weight mixture with carrier liquid, has a break point on a semi-logarithmic viscosity vs. temperature curve at between 3.8×10^3 centipoise and a value below 5.3×10^5 centipoise and a temperature of below 68° C, more preferably below 65° C. In preferred embodiments of the invention, the toner particle polymer is comprised of two or more polymers.

Preferably one of the polymers comprises a first, relatively higher viscosity material in an amount of between 70 and 90 percent and a second polymer having a second, relatively lower viscosity in an amount of between 5 and 25 percent. In some preferred embodiments of

the invention, a third polymer having a relatively low viscosity is comprised in the toner polymer in an amount between 2 and 10 percent. In preferred embodiments of the invention, the third polymer is reactive with components of a substrate on which the toner is printed.

The present inventors have found that under conditions in which the amount of pigment in the toner is increased over that in prior art (and thus thinner layers of toner are utilized) and/or in which the amount of liquid is reduced by removing liquid from toner prior to its transfer, and/or in which the speed of the process is increased and the time available for transfer to the paper decreased, the optimum viscosity is reduced over that of toners of the prior art.

5

10

15

20

25

30

An aspect of some preferred embodiments of the invention relates to a toner including a polymer material that is reactive with a substrate on which it is printed.

In general, printing with toner materials on paper is relatively straightforward, especially when transfer thereto is by heat and pressure, since the toner is forced into the paper and forms a good bond with it.

Thus, in a preferred embodiment of the invention the polymers utilized include a minor proportion of a first polymer having a relatively greater reactive affinity for the paper and a major portion of a second polymer having substantially no reactive affinity or a relatively smaller reactive affinity of the paper. In preferred embodiments of the invention, the first polymer comprises between 2-10% of the total amount of polymer in the toner particles. In some preferred embodiments of the invention, the second polymer is a mixture of polymers.

In one preferred embodiment of the invention the first polymer has an anhydride functionality and is compatible (forms a homogeneous mixture) with the other toner polymers in the particles. The anhydride functionality is believed to form a bond, at the fixing temperature of about 70-90°C, with the cellulose in the paper. In particular, it is believed that the oxygen in the anhydride bonds with hydrogen in the cellulose. Thus, under high speed printing conditions, the anhydride (or other material with a high affinity for paper) provides for adequate boding of the toner to the paper, despite the relatively shorter times available for transfer of the toner to the paper and for fusing it thereto.

The first polymer may be in the form of a terpolymer containing an anhydride functionality, such as maleic anhydride terpolymer or it may, for example, be maleic anhydride grafted linear low density polyethylene, maleic anhydride grafted polypropylene copolymer, maleic anhydride grafted linear ethylene acetate polymer. Other materials with anhydride functionality may also be used.

Other minor portion polymers believed to work in a similar manner include polymers having an epoxy functionality. It is believed that when activated by water or hydroxyl functionalities in the paper, the epoxy functionality bonds with hydroxyl functionalities in the paper.

While the second polymer may include any polymer or mixture of polymers having suitable viscosity, solvation and other parameters for toner, some especially suitable first polymer materials include, ethylene methacrylic acid copolymers and their ionomers, ethylene acrylic acid copolymers and their ionomers, polyamides, etc., or mixtures thereof. It should be understood that some of these materials may have higher or low than optimal viscosity and that blends of the polymers may be required to provided a desired viscosity.

There is thus provided, in accordance with a preferred embodiment of the invention, a liquid toner comprising:

a carrier liquid; and

5

10

15

20

25

30

toner particles dispersed in the carrier liquid, said toner particles comprising:

a polymer blend comprising:

a first polymer comprising a minor portion of said blend and having a relatively higher chemical reactivity with paper; and

a second polymer comprising a major portion of said blend and having a relatively lower or null chemical reactivity with paper.

Preferably, the polymer blend has, on a semi-logarithmic viscosity vs. temperature cooling curve, a transition at a temperature below about 65°C, wherein at temperatures below the transition temperature, the rate of change of viscosity with temperature is higher than the rate of change at temperatures above the transition temperature.

Preferably, at the transition temperature, the viscosity is below about 10⁷ centipoise.

Preferably, at the transition temperature, the viscosity is below about $2x10^5$ centipoise.

Preferably, at the transition temperature, the viscosity is above about 10⁴ centipoise.

In a preferred embodiment of the invention the second polymer comprises at least two polymers.

In a preferred embodiment of the invention, the polymer blend is substantially insoluble in the carrier liquid and wherein at least one of the polymers solvates the carrier liquid at an elevated temperature.

In a preferred embodiment of the invention, the proportion of the first polymer in the blend is between about 2% and about 10%, preferably about 5%.

In a preferred embodiment of the invention, the first polymer comprises a polymer having an anhydride functionality. The first polymer may include, in accordance with various preferred embodiments of the invention, one or more of maleic anhydride terpolymer, maleic anhydride grafted linear low density polyethylene, maleic anhydride grafted polypropylene copolymer, and maleic anhydride grafted linear ethylene acetate polymer.

In preferred embodiments of the invention, the second polymer comprises one or more of ethylene methacrylic acid copolymer; an ionomer of ethylene methacrylic acid copolymer, an ester of ethylene methacrylic acid copolymer, low molecular weight ethylene acrylic acid copolymer, an ionomer of low molecular weight ethylene acrylic acid copolymer, an ester of ethylene acrylic acid copolymer, and an acid modified ethylene vinyl acetate terpolymer.

Preferably, the toner particles comprise at least one pigment.

There is further provided, in accordance with a preferred embodiment of the invention, a liquid toner comprising:

a carrier liquid; and

5

10

15

20

25

30

toner particles dispersed in the carrier liquid, said toner particles comprising:

a polymer blend comprising at least first and second distinct polymers, wherein the polymer blend has, on a semi-logarithmic viscosity vs. temperature cooling curve, a transition at a temperature below about 65°C, wherein at temperatures below the transition temperature, the rate of change of viscosity with temperature is higher than the rate of change at temperatures above the transition temperature.

In a preferred embodiment of the invention, the transition temperature, the viscosity is below about 10^7 centipoise. Preferably, at the transition temperature, the viscosity is below about $2x10^5$ centipoise.

In a preferred embodiment of the invention, at the transition temperature, the viscosity is above about 10⁴ centipoise.

In a preferred embodiment of the invention, the polymer blend is substantially insoluble in the carrier liquid and wherein at least one of the polymers solvates the carrier liquid at an elevated temperature.

In a preferred embodiment of the invention, the polymer blend comprises one or more of ethylene methacrylic acid copolymer, an ionomer of ethylene methacrylic acid copolymer, an ester of ethylene methacrylic acid copolymer, low molecular weight ethylene acrylic acid copolymer, an ionomer of low molecular weight ethylene acrylic acid copolymer, an ester of ethylene acrylic acid copolymer, or an acid modified ethylene vinyl acetate terpolymer.

Preferably, the toner particles comprise at least one pigment.

There is further provided, in accordance with a preferred embodiment of the invention, a method of printing comprising:

providing an electrostatic image; and

5

10

15

20

25

30

developing the electrostatic image with a toner in accordance with any of the preceding claims.

Preferably, the method includes transferring the developed image from a surface on which it is developed to a final substrate.

Preferably, the final substrate contains cellulose.

In a preferred embodiment of the invention, the developed image comprises first transferring the image to an intermediate transfer member and then transferring the image therefrom to the final substrate.

In a preferred embodiment of the invention, transferring comprises fixing the transferred image to the final substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more clearly understood from the following description of the preferred embodiments thereof, taken together with the following drawings, in which:

Fig. 1 shows a semi log plot of viscosity in centipoise as a function of temperature of a melt viscosity cooling curve of two toners, in accordance with a preferred embodiment of the invention; and

Fig. 2 is a schematic drawing of a liquid toner printing system utilizing a toner in accordance with a preferred embodiment of the invention.

<u>DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION</u> NON-LIMITING EXAMPLES OF TONERS

A first exemplary toner, in accordance with a preferred embodiment of the invention, can be prepared by loading 1020 grams of Nucrel 699 resin (an ethylene methacrylic acid copolymer by Dupont), 120 grams of AC5120 resin (an ethylene acrylic acid copolymer by Allied Signal) with 60 grams of Lotadar 8200 (maleic anhydride terpolymer by Atochem) and 1800 grams of Isopar-L (Exxon) an isopparaffinic hydrocarbon fraction in a Ross double planetary mixer, preheated by a heating bath, set to 150°C. The ingredients are mixed for about 1.5 hours at speed control setting 3. The speed is increased to a speed setting of 6 for 30 minutes, the heating is stopped and the mixer is cooled with a fan while mixing is continued.

5

10

15

20

25

30

The result is a pasty material. It is noted, for the reasons given in the summary, that the maleic anhydride has a higher affinity for paper than do the other polymers.

836.30 grams of the pasty material are loaded into a 1S attritor (Union Process) with 3/16" chrome steel grinding media, together with 67.07 grams of Helliogen Blue pigment 7080 (BASF), 7.45 grams of Helliogen Green pigment (BASF), 4.14 grams of aluminum stearate (Riedel de Haen) and 1384.07 grams of Isopar L. The material is ground at 40°C for 20 hours. The result is discharged from the attritor and mixed with an amount of Isopar L to form a working dispersion. The toner is charged utilizing a charge director, preferably a charge director described in the above referenced US patent 5,346,796 and containing 30 parts by weight lecithin, 30 parts by weight Basic Barium Petronate (BBP) and 6 parts by weight isopropylamine dodecylbenzesulfonate (ICI G3300B) as a stabilizer. The charge director, dissolved in Isopar-L is added in an amount of about 30-40 mg of solids of the charge director per gram of toner solids. A small amount of Marcol 82, such as 2% of the carrier liquid, may be added to carrier liquid to form a mixed carrier liquid, as described in the above references.

The result is a cyan toner having a relatively high pigment concentration.

A second exemplary toner, in accordance with a preferred embodiment of the invention, can be prepared by loading 960 grams of Nucrel 699 resin (an ethylene methacrylic acid copolymer by Dupont), 240 grams of AC5120 resin (an ethylene acrylic acid copolymer by Allied Signal) 1800 grams of Isopar-L (Exxon) in a Ross double planetary mixer, preheated by a heating bath, set to 150°C. The ingredients are mixed for about 1.5 hours at speed control setting 3. The speed is increased to a speed setting of 6 for 30 minutes, the heating is stopped and the mixer is cooled with a fan while mixing is continued. The result is a pasty material.

971.75 grams of the pasty material are loaded into a 1S attritor (Union Process) with 3/16" chrome steel grinding media, together with 55.66 grams of Helliogen Blue pigment 7080 (BASF), 4.14 grams of Helliogen Green pigment (BASF), and 11.5 grams of aluminum stearate (Riedel de Haen) and 1257 grams of Isopar L. The material is ground at 58°C for about 1.5 hours, followed by continued grinding at 45°C for 10.5 hours. The result is discharged from the attritor and mixed with an amount of Isopar L to form a working dispersion at about 2% solids. The toner is charged utilizing a charge director, preferably a charge director described in the above referenced US patent 5,346,796 and containing 30 parts by weight lecithin, 30 parts by weight BBP and 15 parts by weight G3300 as a stabilizer. The charge director, dissolved in Isopar-L is added in an amount of about 30-40 mg of solids of the charge director per gram of toner solids.

The result is a cyan toner having a relatively high voltage stability, for use in high speed printing. For black toner an additional 2.5 mg/gm of stabilizer is added.

Fig. 1 shows viscosity as a function of temperature (cooling curves) for the polymer materials used in the two toners. Curve 1, is for the polymer material in the first exemplary toner and curve 2 is for the polymer materials in the second exemplary toner. It is seen that these materials have a break-point at about 45°C and 1.05x10⁴ centipoise and at about 55°C and 10⁴ centipoise, respectively, when mixed with Isopar-L in a 40% w/w concentration.

In general, while, in the past toners with a higher viscosity at these standard conditions was desirable, the lower viscosity toners, as described herein, work well in environments in which the solids concentration is higher at transfer to the paper (for example due to increased evaporation of carrier liquid) or in which the time allotted for transfer is greatly reduced.

10

15

20

25

30

It will be further understood that many variations of the toners according to the invention are possible and the toners that are defined by the claims may be produced using a wide variety of polymers. In particular, other ethylene methacrylic acid copolymers and ionomers and esters of ethylene methacrylic acid copolymers of various molecular weights may be used in place of Nucrel 699. In some preferred embodiments of the invention low molecular weight ethylene acrylic acid copolymers and/or their ionomers and esters and/or other terpolymers such as an acid modified ethylene vinyl acetate terpolymer (ELVAX) may be substituted for the specific AC 5120 resin indicated above. In some preferred embodiments of the invention the polymer having a relatively greater reactive affinity for cellulose can be any suitable polymer having an anhydride or epoxy functionality or other polymer that strongly bonds chemically to paper, preferably to hydrogen or to hydroxyl functionalities of the cellulose. Examples of materials with anhydride functionalities believed to be suitable for use in the present invention include a terpolymer containing an anhydride functionality, maleic anhydride grafted linear low density polyethylene, maleic anhydride grafted polypropylene copolymer, and maleic anhydride grafted linear ethylene acetate polymer.

Figure 2 shows a high speed printer for which the first exemplary toner is designed. This system is described in detail in PCT application PCT/IL98/00553. The reader is referred to that application for more details on the operation of the printer.

Printer 200 of Fig. 2, utilizes a single photoreceptor 102 and a single intermediate transfer member (ITM) 110. However, situated about photoreceptor 102 are a plurality of developers 108. Each developer develops an electrostatic image on photoreceptor 102 with a different color image. The images are transferred seriatim to an intermediate transfer member

110. In a preferred embodiment of the invention, a sheet 48 on an impression roller 42 rotates once for each color and the different color images are transferred to the sheet seriatim. Preferably, photoreceptor 102 is large enough so that a plurality or all of the individual color images are developed during a single rotation of photoreceptor 102. Alternatively, the images are transferred seriatim to the intermediate transfer member and then transferred together to the sheet. In this type of one-shot transfer, the sheet travels at the process speed, but is printed on only once. The developer (which is preferably of the type described in WO 93/01531 or in WO 95/10801) and other components of the printing engine are described with reference to Figs. 11-13 of the '553 application. Other printing engines, as for example those shown in Figs. 2-5 of the '553 application can also be used.

In the embodiment for which the first exemplary toner was described, the process speed is 122 cm/sec and the surface temperature of the intermediate transfer member is between 95 and 100°C. A fan optionally blows air on the image on the ITM to increase the solids concentration prior to transfer from the ITM. In order to assure good transfer from the intermediate transfer member in the approximately 1 cm nip between the ITM and the impression roller the an exemplary pressure of about 6.4 kg/cm² is applied. In addition, to assure transfer of the toner to the intermediate transfer member an exemplary transfer voltage of about 650 Volts is used.

10

15

20

25

30

The second exemplary toner is useful in conjunction with more conventional systems as described in the above referenced patents and applications, in which a same conventional roller developer is used for developing all of the separations and a low toner particle concentration liquid toner (such as 2%) is introduced in the space between the developer roller and the . In this system, the process speed is about 61 cm/sec and the pressure is about 5 kg/cm². The transfer voltage is about 650 Volts. The interested reader is directed to these publications for further details.

It will be understood that, in view of the results presented herein and in WO 92/17823 (USSN 08/203,597), breakpoints in the standard cooling curve for useful toner polymers, may vary, depending on the printing conditions, occurring between 10⁴ (or less) centipoise to above 10⁷ centipoise. Preferably, of course, the temperature is below 65°C, more preferably 60°C or below.

It will be understood that the particular materials and proportions of materials are provided for exemplary purposes only. As is well known in the art, the proportions, temperatures, mixing times and grinding times as well as the choice of charge director can be

varied substantially in the production of liquid toner. Furthermore, while a number of different embodiments have been shown, details of one embodiment of the invention may, where applicable, in other embodiments of the invention. Similarly, some details shown in the embodiments, while preferred, are not essential and some preferred embodiments of the invention may omit them.

As used herein, the terms "have", "include" and "comprise" or their conjugates, as used herein mean "including but not limited to".

CLAIMS

1.	А	liand	toner	comprising:
1.	4 1	114010		00pog.

a carrier liquid; and

toner particles dispersed in the carrier liquid, said toner particles comprising:

a polymer blend comprising:

a first polymer comprising a minor portion of said blend and having a relatively higher chemical reactivity with paper; and

a second polymer comprising a major portion of said blend and having a relatively lower or null chemical reactivity with paper.

10

- 2. A liquid toner according to claim 1 wherein the polymer blend has, on a semi-logarithmic viscosity vs. temperature cooling curve, a transition at a temperature below about 65°C, wherein at temperatures below the transition temperature, the rate of change of viscosity with temperature is higher than the rate of change at temperatures above the transition temperature.
- 3. A liquid toner according to claim 2 wherein at the transition temperature, the viscosity is below about 10⁷ centipoise.

20

- 4. A liquid toner according to claim 3 wherein at the transition temperature, the viscosity is below about $2x10^5$ centipoise.
- 5. A liquid toner according to any of claims 2-4 wherein at the transition temperature, the viscosity is above about 10⁴ centipoise.
 - 6. A liquid toner according to any of the preceding claims wherein the second polymer comprises at least two polymers.
- 30 7. A liquid toner according to any of the preceding claims wherein the polymer blend is substantially insoluble in the carrier liquid and wherein at least one of the polymers solvates the carrier liquid at an elevated temperature.

8. A liquid toner according to any of the preceding claims wherein the proportion of the first polymer in the blend is between about 2% and about 10%.

9. A liquid toner according to claim 8 wherein the proportion is about 5%.

5

- 10. A liquid toner according to any of the preceding claims wherein the first polymer comprises a polymer having an anhydride functionality.
- 11. A liquid toner according to any of the preceding claims wherein the first polymer comprises maleic anhydride terpolymer.
 - 12. A liquid toner according to any of the preceding claims wherein the first polymer comprises maleic anhydride grafted linear low density polyethylene.
- 15 13. A liquid toner according to any of the preceding claims wherein the first polymer comprises maleic anhydride grafted polypropylene copolymer.
 - 14. A liquid toner according to any of the preceding claims wherein the first polymer comprises maleic anhydride grafted linear ethylene acetate polymer.
 - 15. A liquid toner according to any of the preceding claims wherein the second polymer comprises ethylene methacrylic acid copolymer.
- 16. A liquid toner according to any of the preceding claims wherein the second polymer comprises an ionomer of ethylene methacrylic acid copolymer.
 - 17. A liquid toner according to any of the preceding claims wherein the second polymer comprises an ester of ethylene methacrylic acid copolymer.
- 30 18. A liquid toner according to any of the preceding claims wherein the second polymer comprises low molecular weight ethylene acrylic acid copolymer.

19. A liquid toner according to any of the preceding claims wherein the second polymer comprises an ionomer of low molecular weight ethylene acrylic acid copolymer.

- 20. A liquid toner according to any of the preceding claims wherein the second polymer comprises an ester of ethylene acrylic acid copolymer.
 - 21. A liquid toner according to any of the preceding claims wherein the second polymer comprises an acid modified ethylene vinyl acetate terpolymer.
- 10 22. A liquid toner according to any of the preceding claims wherein the toner particles comprise at least one pigment.
 - 23. A liquid toner comprising:

a carrier liquid; and

20

30

toner particles dispersed in the carrier liquid, said toner particles comprising:

a polymer blend comprising at least first and second distinct polymers, wherein the polymer blend has, on a semi-logarithmic viscosity vs. temperature cooling curve, a transition at a temperature below about 65°C, wherein at temperatures below the transition temperature, the rate of change of viscosity with temperature is higher than the rate of change at temperatures above the transition temperature.

- 24. A liquid toner according to claim 23 wherein at the transition temperature, the viscosity is below about 10⁷ centipoise.
- 25. A liquid toner according to claim 24 wherein at the transition temperature, the viscosity is below about 10⁵ centipoise.
 - 26. A liquid toner according to any of claims 23-25 wherein at the transition temperature, the viscosity is above about 10⁴ centipoise.
 - 27. A liquid toner according to any of claims 23-25 wherein the polymer blend is substantially insoluble in the carrier liquid and wherein at least one of the polymers solvates the carrier liquid at an elevated temperature.

28. A liquid toner according to any of claims 23-27 wherein the polymer blend comprises ethylene methacrylic acid copolymer.

- 5 29. A liquid toner according to any of claims 23-28 wherein the polymer blend comprises an ionomer of ethylene methacrylic acid copolymer.
 - 30. A liquid toner according to any of claims 23-29 wherein the polymer blend comprises an ester of ethylene methacrylic acid copolymer.
- 31. A liquid toner according to any of claims 23-30 wherein the polymer blend comprises low molecular weight ethylene acrylic acid copolymer.
- 32. A liquid toner according to any of claims 23-31 wherein the polymer blend comprises an ionomer of low molecular weight ethylene acrylic acid copolymer.
 - 33. A liquid toner according to any of claims 23-32 wherein the polymer blend comprises an ester of ethylene acrylic acid copolymer.
- 20 34. A liquid toner according to any of claims 23-33 wherein the polymer blend comprises an acid modified ethylene vinyl acetate terpolymer.
 - 35. A liquid toner according to any of claims 23-34 wherein the toner particles comprise at least one pigment.

36. A method of printing comprising:

10

25

30

providing an electrostatic image; and

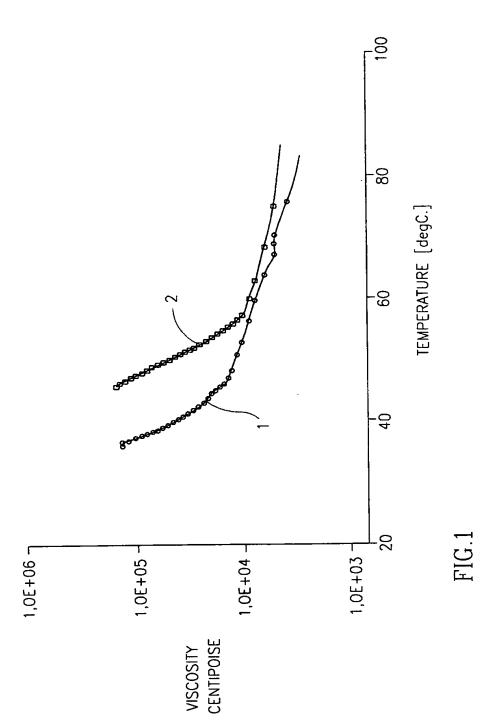
developing the electrostatic image with a toner in accordance with any of the preceding claims.

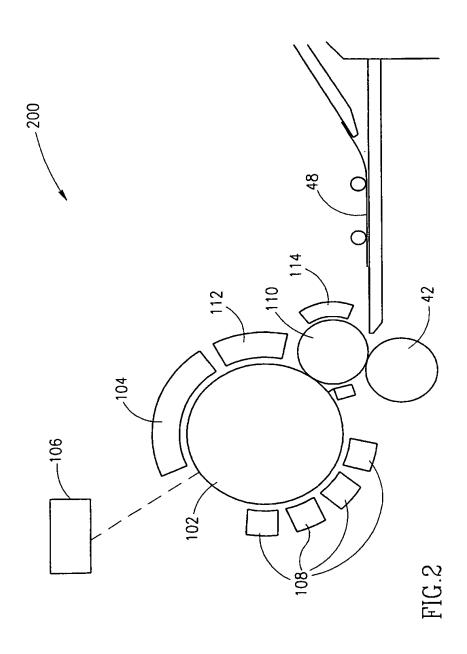
37. A method according to claim 36 and including transferring the developed image from a surface on which it is developed to a final substrate.

38. A method according to claim 37 wherein the final substrate contains cellulose.

- 39. A method according to claim 37 wherein the final substrate is a paper.
- 5 40. A method according to any of claims 37-39 wherein transferring the developed image comprises first transferring the image to an intermediate transfer member and then transferring the image therefrom to the final substrate.
- 41. A method according to any of claims 37-40 wherein transferring comprises fixing the transferred image to the final substrate.

1/2





INTERNATIONAL SEARCH REPORT

		PCT/IL	. 00/00031
A. CLASSI IPC 7	FICATION OF SUBJECT MATTER G03G9/13	· · · · · ·	
According to) International Patent Classification (IPC) or to both national classifica	tion and IPC	
	SEARCHED	ING TELEVITO	
	cumentation searched (classification system followed by classification	on symbols)	
IPC 7	G03G		
Documentat	ion searched other than minimum documentation to the extent that s	uch documents are included in the fi	elds searched
	ata base consulted during the international search (name of data bas ta, PAJ, EPO-Internal	le and, where practical, search term	ıs used)
C DOCUM	ENTS CONSIDERED TO BE RELEVANT		
Category *	Relevant to claim No.		
X	US 5 759 733 A (K.TSUBUKO) 2 June 1998 (1998-06-02)		1,10-22
Y	column 3, line 21 - line 22 column 3, line 24 - line 25 column 4, line 18 - line 36		2-5
x	DATABASE WPI Section Ch, Week 198931 Derwent Publications Ltd., London Class A04, AN 1989-223001 XP002147328	1	
Υ	& JP 01 145666 A (RICOH) abstract		2-5
х	GB 2 029 040 A (RICOH) 12 March 1980 (1980-03-12)		1
Y	page 2, line 102 - line 107; clai example 5	2-5	
	·	/	
	her documents are listed in the continuation of box C.	X Patent family members are	e listed in annex.
"A" docume consider filing of "L" docume which citatio "O" docume other "P" docume later ti	ent defining the general state of the art which is not dered to be of particular relevance document but published on or after the international faite ent which may throw doubts on priority claim(s) or is cited to establish the publication date of another nor other special reason (as specified) ent referring to an oral disclosure, use, exhibition or means ent published prior to the international filing date but han the priority date claimed	To later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family	
	actual completion of the international search	Date of mailing of the internation $26/09/2000$	nal search report
<u></u>	4 September 2000		
Name and	mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (-31-70) 340-2040, Tx. 31 651 epo ni, Fax: (+31-70) 340-3018	Authorized officer Vanhecke, H	

INTERNATIONAL SEARCH REPORT

Interr. nal Application No PCT/IL 00/00031

		PC1/1L 00/00031		
C.(Continu	NOCUMENTS CONSIDERED TO BE RELEVANT			
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Х	DD 241 491 A (VEB FILMFABRIK WOLFEN) 10 December 1986 (1986-12-10) claim 1	1		
X	WO 92 17823 A (SPECTRUM SCIENCES) 15 October 1992 (1992-10-15)	23-41		
Y	claims 1-10 	2–5		
A	US 3 869 397 A (J.C.TRISTAN TELLIER) 4 March 1975 (1975-03-04) claims 1-7	. 1		
X	US 5 330 872 A (P.E.MATERAZZI) 19 June 1994 (1994-06-19) claim 1; examples 1-10	1		
	·			

INTERNATIONAL SEARCH REPORT

information on patent family members

Intern .ai Application No PCT/IL 00/00031

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5759733	A	02-06-1998	JP 2000883 A JP 2806950 B	05-01-1990 30-09-1998
JP 1145666	Α	07-06-1989	NONE	
		12 02 1000		
GB 2029040	^	12-03-1980	JP 1180605 C JP 55033110 A	09-12-1983 08-03-1980
			JP 58009419 B	21-02-1983
			DE 2935287 A	06-03-1980
			US 4264699 A	28-04-1981
DD 241491	A	10-12-1986	NONE	
WO 9217823	Α	15-10-1992	CA 2106864 A	29-09-1992
			DE 69217046 D	06-03-1997
			DE 69217046 T	24-07-1997
			EP 0577688 A HK 70797 A	12-01-1994 06-06-1997
			JP 3007156 B	07-02-2000
			JP 7500922 T	26-01-1995
			SG 49132 A	18-05-1998
US 3869397	Α	04-03-1975	AU 6107973 A	10-04-1975
			BE 806713 A	15-02-1974
			DE 2354259 A	09-05-1974
			GB 1439626 A JP 49110349 A	16-06-1976
			NL 7314145 A,B,	21-10-1974 03-05-1974
US 5330872		 19-07-1994	US 5116705 A	 26-05-1992
			US 5238762 A	24-08-1993
			AU 7497891 A	21-10-1991
			DE 69119760 D	27-06-1996
			DE 69119760 T	16-01-1997
			EP 0523071 A WO 9114974 A	20-01-1993
			WO 9114974 A US 5240806 A	03-10-1991 31-08-1993
			US 5275906 A	04-01-1994
	•		AU 2574892 A	27-04-1993
			EP 0700535 A	13-03-1996
			JP 6511323 T	15-12-1994
			WO 9306531 A	01-04-1993